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ELLIPSOMETRIC MEASUREMENT OF LIQUID FILM THICKNESS

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ELLIPSOMETRIC MEASUREMENT OF LIQUID FILM THICKNESS

Introduction

During the later period of this research project (NAG8-045) the system of two components, water and succinonitrile, has been subjected to ellipsometric measurement of liquid film thickness at several temperatures for a few concentrations.

The experiment was to indirectly estimate the surface pressure of a liquid for a binary monotectic system. The procedure requires determination of the critical wetting temperature for the system by applying Young's equation which describes the relationship among the interfacial free energies:

$$\gamma(L_2S) = \gamma(L_1S) + \gamma(L_1L_2)\cos\theta$$

where θ is the contact angle and γ is the interfacial energy corresponding to the interface denoted by the liquid L and solid S phases. L_1 and L_2 refer to liquid 1 and liquid 2, respectively. The liquid film from the solutions may be formed by condensation of the vapor or by van der Waals adsorption of the liquid along the container wall. Thus it becomes necessary to estimate partial pressures of each component for each binary solution equilibrated at different temperatures.

Experiment

Since ellipsometric measurement of film thickness requires refractive indices of medium, liquid and substrate, it is absolutely imperative that these values be available or estimated accurately at a particular wavelength, in our case, 632.8 nm of He-Ne laser. Unfortunately these quantities are not available and our major task has been to determine the refractive indices of the solutions at several temperatures with some degree of accuracy.

Refractive indices are very sensitive to temperature and composition of the liquid. Therefore, index measurements were made

using two different devices, a prism spectrometer and an ellipsometer, with He-Ne laser for both instruments. The results from the two were comparable within experimental errors. The values are shown in the accompanying tables.

Table 1. Refractive Indices of Succinonitrile-rich Phase

T ^o C	Ellipsometer	Prism Spectrometer
18.2	1.42114	
19.2		1.42043
19.6		1.42069
19.9	1.41871	
21.0		1.42017
22.0		1.41945
24.0	1.41990	
24.6		1.41763
25.5		1.41661
26.0	1.42003	
28.0	1.41416	
29.0	1.41135	
30.0	1.41096	
31.0	1.41036	

For the ellipsometric work, prism cells of three different angles of incidence were specifically designed for refractive index and thickness measurements. Refractive indices of water estimated ellipsometrically are compared with those from the literature¹. As seen in Table 2, the agreement between the two is excellent near room temperature. At temperatures far from room temperature it becomes difficult to control temperature within the glass cell.

Table 2. Refractive Indices of Water

T° C	Ellipsometer	Ref. 1 [*]	Deviation %
16.0	1.32880	1.33245	0.3
18.0	1.32977	1.33229	0.2
22.0	1.33197	1.33194	0.002
25.0	1.33119	1.33165	0.03
29.0	1.33099	1.33121	0.02
40.0	1.32970	1.32977	0.005

*Temperature was rounded to 3 digits for this table.

Preliminary Result

Liquid film thicknesses from water-rich and succinonitrile-rich phases show variation of thickness with temperature. Variations are small between 21° C and 23° C. The two layers give rise to the same thickness near the monotectic temperature. As the temperature is raised beyond room temperature increasing fogging becomes a serious problem.

In our calculation of film thickness, our experimental values of refractive index were used. The indices were measured usually on a large drop of the phase placed at the floor corner away from the prism wall to minimize capillary migration of the liquid along the wall. Condensation of vapor on the wall is the main mechanism of film formation when the wall is not in contact with the sample solution.

The variation of the index with temperature for both conjugate phases of each succinonitrile-water solution is as anticipated because at higher temperatures there will be more homogeneous mixing between the two immiscible components. This trend was shown by both the hollow-prism spectrometer and the ellipsometer.

Conclusion

Much work remains to be done including more precise control of the sample cell temperature and accurate measurement of film thickness with a fully automated ellipsometer system. Automation of measurement is especially critical because temperature control is not easy and the constant temperature is only in a short span. The automated system will require anew design of prism cells so that the difficulty of observing liquid film formation on the vertical wall can be eliminated. The liquid film itself on the cell ceiling will be less dependent on any capillary adsorption of liquid. Partial pressures and composition of each component vapor phase should also be estimated.

Acknowledgements

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References

1. Stanley, E. M.; J. Chem. Eng. Data, 16, 454 (1971)